

TITLE: UNDERSTANDING OLIVINE CO₂ MINERAL SEQUESTRATION MECHANISMS
AT THE ATOMIC LEVEL: OPTIMIZING REACTION PROCESS DESIGN

PIs: M.J. McKelvy,* R.W. Carpenter, R. Sharma, and G. H. Wolf

STUDENTS: Hamdallah Béarat

INSTITUTION: Arizona State University
Center for Solid State Science and
Science and Engineering of Materials Graduate Program
Tempe, AZ 85287-1704
* Phone: (480) 965-4535; FAX: (480) 965-9004; E-mail: mckelvy@asu.edu

SUBCONTRACTOR: None

INDUSTRY

COLLABORATOR: None

GRANT NO.: DE-FG26-01NT41282

PERIOD OF

PERFORMANCE: Sept. 20, 2001 – Sept. 19, 2002

DATE: March 2002

ABSTRACT

INTRODUCTION

Fossil fuels, especially coal, can support global energy demands for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide permanent and environmentally benign CO₂ sequestration. The primary challenge remaining for CO₂ mineral sequestration is economically viable process development. Aqueous carbonation of widely available Mg-rich minerals, such as olivine, is a leading process candidate, which generates the stable, naturally occurring mineral magnesite (MgCO₃). Enhancing the carbonation reaction rate and its degree of completion are key to developing an economically viable process. The objective of this project is to use advanced analytical techniques, including the first application of environmental-cell (E-cell) high-resolution transmission electron microscopy (HRTEM), to identify the key interface mechanisms that govern aqueous solution, mineral carbonation reaction kinetics. Use of H₂O (g) and CO₂ (g) in the E-cell is essential to enhance the electron beam stability of reaction intermediates/products for HRTEM observation. The project goal is to develop the necessary understanding to engineer enhanced carbonation materials and processes for CO₂ disposal.

ACCOMPLISHMENTS TO DATE

The first half of this one-year project has focused on (1) obtaining high-purity single and polycrystalline samples of naturally occurring olivine, with different levels of Fe substitution, (2) phase and compositional sample characterization, and (3) developing the necessary techniques to prepare and

preparing suitable samples for E-cell HRTEM investigation of the interface mechanisms that govern aqueous olivine mineral carbonation. The second half of this project will focus on the investigation of the interface reaction mechanisms that govern aqueous mineral carbonation.

We have successfully collected and characterized olivine (forsterite) single crystal and polycrystalline materials, which contain different Fe levels. The samples selected for investigation include several purchased samples and a variety of materials collected during field trips to the Peridot Mine on the San Carlos Indian Reservation, Gila County, AZ. The primary materials to be used in these studies are the above collected samples, which include light green (LG) and grey green (GG) samples, with the grey green samples having a higher Fe content. Analysis of materials suitability for this project involved structural, elemental, and textural characterization: (1) structural: using X-ray powder diffraction (XPD), (2) elemental: using particle induced X-ray emission (PIXE) and electron microprobe analysis (EMPA), and (3) textural: using polarized light microscopy (PLM).

Structural analysis (XPD): The XPD patterns for the light and grey green samples indicate they are pure olivine/forsterite $[(\text{Mg,Fe})_2\text{SiO}_4]$. The cell parameters for these two samples agree well with those previously reported for Mg-rich forsterite. *Elemental analysis (PIXE and EMPA):* Mg, Si, Fe and O are the only major elements observed. All other elements present were less than 1% by weight in their oxide form. Importantly, the light green and grey green materials have distinctly different Fe compositions, making them well suited for studying the effects of Fe on the solid/solution interface reaction mechanisms that govern mineral carbonation. The chemical formulas for these olivine/forsterite materials are LG: $(\text{Mg}_{0.915} \text{Fe}_{0.085})_2\text{SiO}_4$ and GG: $(\text{Mg}_{0.83} \text{Fe}_{0.17})_2\text{SiO}_4$. *Textural analysis (PLM):* Observation of thin sections via polarized light microscopy shows the polycrystalline materials contain a variety of grain boundaries, providing a range of interface types to probe their roles in aqueous mineral carbonation. The crystalline grains often experience compositional variation (e.g., Fe composition) near their boundaries. Such compositional differences near olivine surfaces and grain boundaries are of particular interest in this project, as they may be associated with the incubation period observed before naturally occurring olivine begins carbonation during aqueous fluid carbonation.

Single crystal samples for E-cell HRTEM analysis of aqueous mineral carbonation reaction intermediates have been successfully prepared via thin sectioning, core-drilling a 3mm thin-section disc, dimpling the disc to perforation, and low voltage ion milling to generate wedge-shaped nanoscale sample edges suitable for mechanistic mineral carbonation reaction investigations. Similar attempts to prepare polycrystalline samples did not succeed, as the samples fragmented at their grain boundaries. A new method to prepare these samples has been developed to maintain their structural integrity during mineral carbonation and subsequent E-cell HRTEM observation. Samples are mounted on glass slides for thin sectioning. After thin sectioning, the olivine surface is bonded to a single crystal silicon wafer using G1 epoxy (Gatan, Inc.), which provides further structural support to the polycrystalline olivine structure. The glass slide is removed with acetone. The sample is dimpled through the Si support and low-voltage ion milled to prepare suitable E-cell HRTEM samples to observe for mechanistic mineral carbonation studies.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Conference Presentations

- M.J. McKelvy, R.W. Carpenter, H. Béarat, G. Wolf, and R. Sharma “Understanding Olivine CO₂ Mineral Sequestration Mechanisms at the Atomic Level: Optimizing Reaction Process Design,” *University Coal Research Contractors Review Conference*, Pittsburgh, Pennsylvania, June 4-5, 2002.

Students Supported under this Grant

- Hamdallah Béarat, graduate (Ph.D.) student in the Science and Engineering of Materials Graduate Program, Arizona State University